

Correlational latent heat by nonlocal kinetic theory

Ludwig Boltzmann
20 Feb 1844 Vienna, Austria
5 Oct 1906 Duino, Italy (Italy)



Sitzungsberichte der Mathematisch-Naturwissenschaftlichen Classe der Kaiserlichen Akademie der Wissenschaften Abteilung IIa, Mathematik, Astronomie, Physik, Meteorologie und Technik, red. 10.10.1872:

$$\frac{\partial f}{\partial t} = \int_0^\infty \int_0^\infty \int_0^\infty \left[\frac{f(\tilde{\varepsilon}_1, t)}{\sqrt{\tilde{\varepsilon}_1}} \frac{f(\tilde{\varepsilon}_2, t)}{\sqrt{\tilde{\varepsilon}_2}} \frac{f(\tilde{\varepsilon}_3, t)}{\sqrt{\tilde{\varepsilon}_3}} \frac{f(\tilde{\varepsilon}_4, t)}{\sqrt{\tilde{\varepsilon}_4}} \right] \times \frac{\partial^2 f}{\partial p \partial q} d\tilde{\varepsilon}_1 d\tilde{\varepsilon}_2 d\tilde{\varepsilon}_3 d\tilde{\varepsilon}_4$$

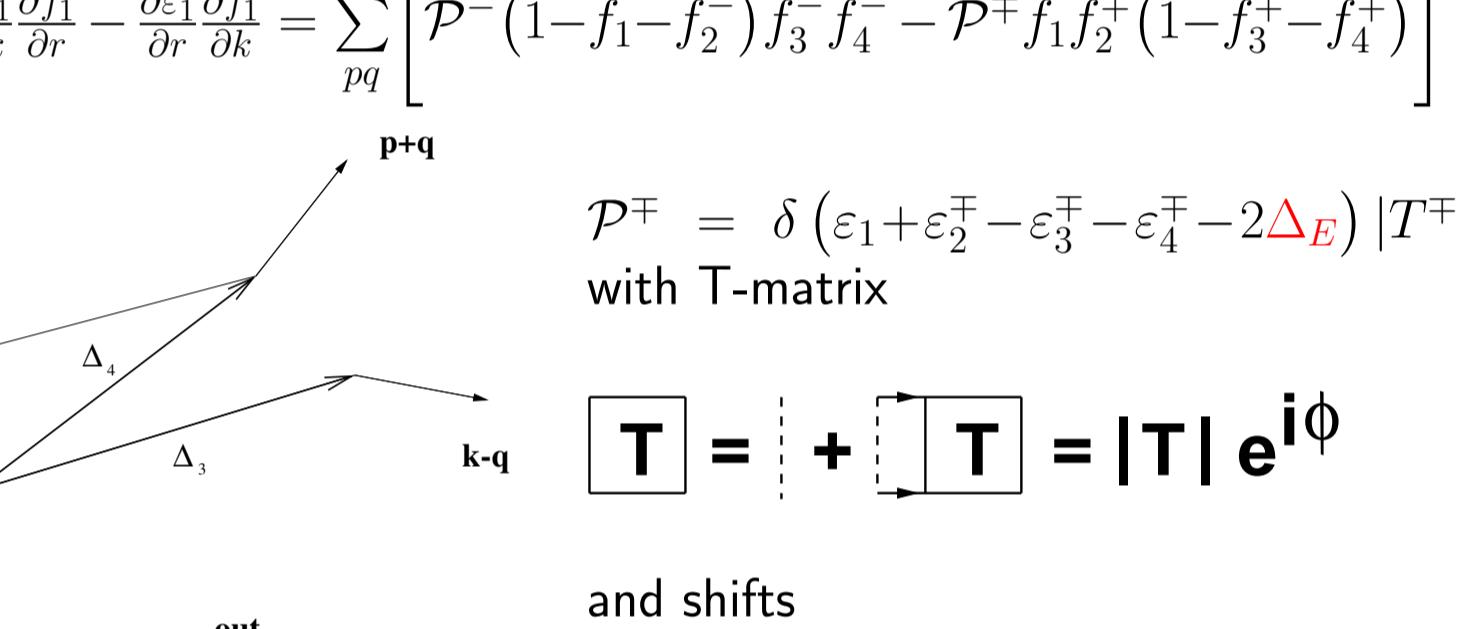
Dies ist die Fundamentalgleichung für die Veränderung Function $f(x, t)$. Ich bemerke nochmal, dass die Wurzeln

$$\frac{\partial f_k}{\partial t} = \sum_{pq} P(f_{k-q} f_{p+q} - f_k f_p)$$

instantaneous in time, local in space

Non-local corrections necessary since virial corrections are missing (Enskog, Bogoliubov, Green, Ernst, Thirring..)

Consistent nonlocal kinetic equation

$$\frac{\partial f_1}{\partial t} + \frac{\partial \varepsilon_1}{\partial k} \frac{\partial f_1}{\partial r} - \frac{\partial \varepsilon_1}{\partial r} \frac{\partial f_1}{\partial k} = \sum_{pq} \left[\mathcal{P}^- (1-f_1-f_2) f_3^- f_4^- - \mathcal{P}^+ f_1 f_2^+ (1-f_3^+ f_4^+) \right]$$


$$\mathcal{P}^+ = \delta(\varepsilon_1 + \varepsilon_2^+ - \varepsilon_3^+ - \varepsilon_4^+ - 2\Delta_E) |T^+|^2$$

with T-matrix

$$T = |\mathbf{T}| e^{i\phi}$$

and shifts

$$\Delta_1 = \frac{\partial \phi}{\partial \Omega} \Big|_{\varepsilon_1+\varepsilon_2}, \quad \Delta_2 = \left(\frac{\partial \phi}{\partial p} - \frac{\partial \phi}{\partial q} - \frac{\partial \phi}{\partial k} \right) \Big|_{\varepsilon_1+\varepsilon_2}$$

where

$$f_1 \equiv f(k, r, t), \quad f_2^- \equiv f(p, r - \Delta_2, t), \quad f_3^- \equiv f(k - q - \Delta_1, r - \Delta_3, t - \Delta_1), \quad f_4^- \equiv f(p + q - \Delta_1, r - \Delta_4, t - \Delta_1)$$

$$\Delta_E = -\frac{1}{2} \frac{\partial \phi}{\partial t} \Big|_{\varepsilon_1+\varepsilon_2}, \quad \Delta_K = \frac{1}{2} \frac{\partial \phi}{\partial r} \Big|_{\varepsilon_1+\varepsilon_2}, \quad \Delta_3 = -\frac{\partial \phi}{\partial k} \Big|_{\varepsilon_1+\varepsilon_2}, \quad \Delta_4 = -\left(\frac{\partial \phi}{\partial p} + \frac{\partial \phi}{\partial q} \right) \Big|_{\varepsilon_1+\varepsilon_2}$$

Nonequilibrium thermodynamics from balance

Quasiparticle parts (Landau theory – like)

$$n^{qp} = \sum_k f, \quad Q^{qp} = \sum_k k f, \quad J^{qp} = \sum_k \frac{\partial \varepsilon}{\partial k} f$$

$$\mathcal{E}^{qp} = \sum_k \left(\frac{k^2}{2m} + \frac{1}{2} \sum_m m f_k \right) f_k, \quad \mathcal{J}_{ij}^{qp} = \sum_k \left(k_j \frac{\partial \varepsilon}{\partial k_i} + \delta_{ij} \varepsilon \right) f - \delta_{ij} \mathcal{E}^{qp}$$

Two-particle correlated parts

$$n^{mol} = \int dP \Delta_t, \quad Q^{mol} = \int dP \frac{k+p}{2} \Delta_t, \quad \mathcal{E}^{mol} = \int dP \frac{\varepsilon_k + \varepsilon_p}{2} \Delta_t$$

$$\mathcal{J}_{ij}^{mol} = \frac{1}{2} \int dP \left\{ k_j \Delta_{3i} + p_j (\Delta_{4i} - \Delta_{2i}) + q_j (\Delta_{4i} - \Delta_{3i}) \right\}$$

Conservation laws

$$\frac{\partial(n^{qp} + n^{mol})}{\partial t} + \frac{\partial(j^{qp} + j^{mol})}{\partial r} = 0$$

$$\frac{\partial(Q_j^{qp} + Q_j^{mol})}{\partial t} + \sum_i \frac{\partial(\mathcal{J}_{ij}^{qp} + \mathcal{J}_{ij}^{mol})}{\partial r_i} = 0$$

$$\frac{\partial(\mathcal{E}^{qp} + \mathcal{E}^{mol})}{\partial t} + \frac{\partial(j_E^{qp} + j_E^{mol})}{\partial r} = 0$$

Probability to form a molecule per time $dP = \delta_{1234} |t_{sc}|^2 f_1 f_2 (1 - f_3 - f_4)$

Entropy balance

$$\frac{\partial(S^{qp} + S^{mol})}{\partial t} + \frac{\partial(j_S^{qp} + j_S^{mol})}{\partial r} = \mathcal{I}_{gain}^S$$

quasiparticle part $S^{qp}(\mathbf{r}, t) = -k_B \sum_a \int \frac{dk}{(2\pi)^3} [f_1 \ln f_1 + (1 \mp f_1) \ln(1 \mp f_1)]$
molecular part $S^{mol} = -\frac{k_B}{2} \sum_{ab} \int dP \ln \frac{f_3 f_4}{(1 \mp f_3)(1 \mp f_4)}$

entropy current $j_S^{qp}(\mathbf{r}, t) = -\frac{k_B}{2} \sum_a \int \frac{dk}{(2\pi)^3} \frac{\partial \varepsilon_1}{\partial k} [f_1 \ln f_1 + (1 \mp f_1) \ln(1 \mp f_1)]$
molecular part $j_S^{mol} = \frac{k_B}{2} \sum_{ab} \int dP \left[\ln \frac{f_2}{(1 \mp f_2)} \Delta_2 - \ln \frac{f_3}{(1 \mp f_3)} \Delta_3 - \ln \frac{f_4}{(1 \mp f_4)} \Delta_4 \right]$

entropy gain $\mathcal{I}_{gain}^S = -\frac{k_B}{2} \sum_{ab} \int dP \ln \frac{f_3 f_4 (1 \mp f_1) (1 \mp f_2)}{(1 \mp f_3) (1 \mp f_4) f_1 f_2} \geq 0$

• H-theorem for nonlocal kinetic theory [Phys. Rev. E 96 \(2017\) 032106](#)

Energy conversion: latent heat

There appear an internal energy- $\mathcal{I}_{gain} = \int dP \Delta_E$ and momentum-gain $\mathcal{F}_{gain} = \int dP \Delta_K$

From nonlocal kinetic equation

$$\int \frac{dk}{(2\pi)^3} \varepsilon_k \frac{\partial f_k}{\partial t} = -\frac{d}{dt} \int dP \frac{\varepsilon_k + \varepsilon_p}{2} \Delta_t + \int dP \Delta_E$$

energy gain combines together with drift term into time derivative

$$\sum_a \int \frac{dk}{(2\pi)^3} \varepsilon_k \frac{\partial f}{\partial t} - \mathcal{I}_{gain}^E = \frac{\partial E^{qp}}{\partial t}.$$

of the quasiparticle energy functional

$$\mathcal{E}^{qp} = \sum_a \int \frac{dk}{(2\pi)^3} f_a(k) \frac{k^2}{2m} + \frac{1}{2} \sum_{ab} \int \frac{dk dp}{(2\pi)^6} f_a(k) f_b(p) \mathcal{T}_{ex}(\varepsilon_1 + \varepsilon_2, k, p, 0)$$

- By energy gain $\Delta_E = \frac{\partial \Phi}{\partial t}$ transformation of kinetic energy into correlation energy. Similar to breathing hard-sphere by Pauli-blocking

Relation to Landau theory

Landau theory works only if collisions \tilde{I} treated instant and local
From kinetic equation $\frac{\partial f_k}{\partial t} = \tilde{I}_k$ follows:

number of particles	energy balance
$\frac{dn}{dt} = \int \frac{dk}{(2\pi)^3} \frac{\partial \tilde{I}_k}{\partial t} = \int \frac{dk}{(2\pi)^3} \tilde{I}_k \equiv 0$	$\frac{dE}{dt} = \int \frac{dk}{(2\pi)^3} \frac{\partial \mathcal{E}}{\partial t} = \int \frac{dk}{(2\pi)^3} \tilde{\mathcal{E}}_k \tilde{I}_k \equiv 0$

Nonlocal kinetic theory

$$\frac{dn}{dt} = \frac{d}{dt} \int \frac{dk}{(2\pi)^3} f_k + \frac{d}{dt} \int dP \Delta_E$$

$$\frac{dE}{dt} = \int \frac{dk}{(2\pi)^3} \varepsilon_k \frac{\partial f_k}{\partial t} + \frac{d}{dt} \int dP \frac{\varepsilon_k + \varepsilon_p}{2} \Delta_t - \int dP \Delta_E$$

Instant approximation, last term can be rewritten $\Delta_E = -\frac{1}{2} \frac{\partial \phi}{\partial t}$

$$-\int dP \Delta_E = \frac{1}{2} \int dP \frac{\partial \phi}{\partial t} = \int \frac{dk}{(2\pi)^3} \int dP \frac{\delta \phi}{\delta \tilde{f}_k} \frac{\partial \tilde{f}_k}{\partial t} \equiv \int \frac{dk}{(2\pi)^3} \varepsilon_k \frac{\partial \tilde{f}_k}{\partial t}$$

with rearrangement energy follows variational expression of Landau theory $\tilde{\varepsilon}_k = \varepsilon_k + \frac{\Delta}{\varepsilon_k}$
Landau theory mimics for energy gain, but no correlated density !

Role of internal gains

Internal energy- and momentum gain $I_E^{gain} = \int dP \Delta_E$ $I_K^{gain} = \int dP \Delta_K$

together with drift exactly into derivative

$$\int \frac{d^3 k}{(2\pi)^3} \varepsilon_k \frac{\partial f}{\partial r_j} - I_K^{gain} = \frac{\partial E^{qp}}{\partial r_j}$$

$$\int \frac{d^3 k}{(2\pi)^3} \varepsilon_k \frac{\partial f}{\partial t} - I_E^{gain} = \frac{\partial E^{qp}}{\partial t}$$

of quasiparticle energy

$$E^{qp} = \int \frac{d^3 k}{(2\pi)^3} f_1(k) \frac{k^2}{2m} + \frac{1}{2} \int \frac{d^3 k d^3 p}{(2\pi)^6} f_1(k) f_2(p) \text{Re } \mathcal{T}(\varepsilon_1 + \varepsilon_2, k, p, 0)$$

instead of Landau functional (limit of $\Delta \rightarrow 0$)

only remaining explicit gain is entropy gain I_S^{gain}

- Internal conversion between correlation and kinetic energy-momentum
- time-dependent Pauli-blocking like vibrating hard spheres

Model of point-like interaction

- T-matrix by s-wave channel with time-dependent scattering length $a_{sc}(t)$
- cold atoms with time-dependent magnetic field near Feshbach resonance
- center-of-the-mass $M = m_a + m_b$, $K = k + p$ and $\mu^{-1} = m_a^{-1} + m_b^{-1}$
- dilute gas the medium effect caused by Pauli blocking negligible

$$\mathcal{T}_R = \frac{2\pi \hbar^2 a_{sc}}{\mu} \frac{1}{1 + i \frac{a_{sc}}{\hbar} \sqrt{2\mu(\Omega - K^2/2M)}}$$

set of Δ s

$$\Delta_t = -\frac{a_{sc} \mu}{\kappa (1 + \frac{a_{sc}}{\hbar} \kappa^2 / \hbar^2)}, \quad \Delta_K = \frac{1}{a_{sc}} \frac{\partial a_{sc}}{\partial r} \frac{\kappa^2}{2\mu} \Delta_t, \quad \Delta_E = -\frac{1}{a_{sc}} \frac{\partial a_{sc}}{\partial t} \frac{\kappa^2}{2\mu} \Delta_t$$

$$\Delta_3 = \Delta_4 = \frac{K}{M} \Delta_t, \quad \Delta_2 = 0$$

- Phys. Rev. E 96 (2017) 032106
- Phys. Rev. B 97 (2018) 195142
- H-theorem for nonlocal kinetic theory [Phys. Rev. E 96 \(2017\) 032106](#)

Thermodynamic quantities

Maxwellian distributions with temperature T and densities of species n_a time-dependent variable $x^2 = 2\pi \frac{a_{sc}^2(t)}{(\mu T)^{3/2}}$ and error function $x\xi(x) = \sqrt{\frac{\pi}{2}} x^2 \text{erfc}(x^{-1})$

correlated density $n^{mol}(x) = n_a n_b \frac{-\pi \hbar^2}{(\mu T)^{3/2}} x^2 \xi'(x) = -2\pi^2 n_a n_b a_{sc}^3 + o(T^2)$
second virial coefficient for hard spheres for low-temperature limit, and $\Pi_{ij}^{mol}(x) = \delta_{ij} T n^{mol}(x)$

quasiparticle energy $E^{qp}(x) = \frac{3}{2} T (n_a + n_b) + 4 T n^{mol}(x)$
three translational degrees of freedom and 8 for correlated molecules (2x3 translational and 2 rotational, classical dumbbell)

molecular energy

$$E^{mol}(x) = \frac{3}{2} n^{mol}(x) T + T x^2 \left(\frac{n^{mol}(x)}{x} \right)' = n^{mol} T \left\{ \frac{1}{2} + \frac{4}{\sqrt{\pi x}} + o(x^{-2}) \right\}$$

in high and low temperature limit brings an additional degree of freedom (two-particle dumbbell state gains an additional third fictitious particle by correlation)

momentum- and energy gains

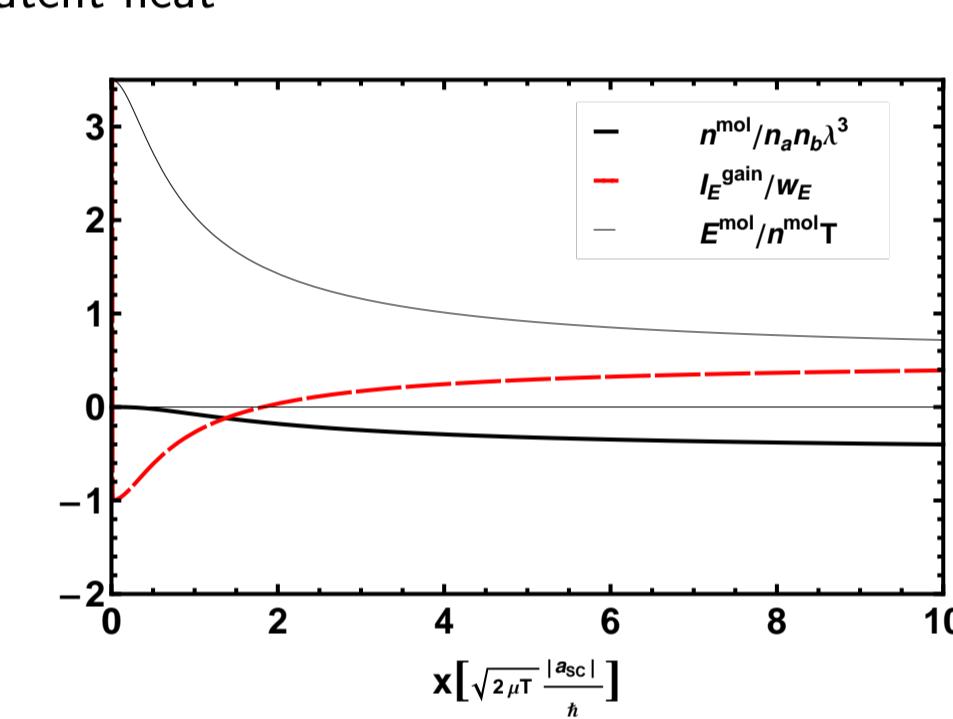
$$I_E^{gain}(x) = 2 T x^2 \left(\frac{n^{mol}(x)}{x} \right)' \left\{ -\frac{\partial a_{sc}}{\partial t} \right\}$$

external power feed due to time-dependent potential $V(t) = \frac{2\pi \hbar^2}{\mu} a_{sc}(t)$ leads to extra feed to the energy balance

$$\frac{\partial E^{qp}}{\partial t} = -I_E^{gain} + 4 T n^{mol} \frac{\partial \ln a_{sc}}{\partial t}$$

Correlational entropy

- energy and entropy gain $I_S^{gain} = I_E^{gain}$
- latent heat is $T \times$ entropy difference during a phase transition
- analogously formation of short-living molecules
- energy gain is the rate of latent heat



energy gain/external power = ratio of latent heat to interaction strength (time-independent)
molecular density
correlation energy (thin line)

- sign change at $x_0 \approx 1.8184$ or $a_{sc}/\lambda \approx 0.7254$ independent of interaction
- scattering length $\times T$ smaller, $I_E^{gain}/w_E = -1 + 3x^2 + o(x)$, **correlational cooling**
- at high temperatures gain approaches half of external power, **correlational heating** [Phys. Rev. B 97 \(2018\) 195142](#)

Summary: Nonequilibrium quantum hydrodynamics

1. Nonlocal kinetic theory recast quantum correlations into nonlocal shifts
 - unifies Landau quasiparticle theory with Enskog theory of dense gases
 - particle-hole vs space-time symmetry completed
 - explicit calculation of Wigner function not necessary, correlated observables directly from nonlocal kinetic equation
 - same computational expense as solving Boltzmann equation
 - balance equation complete with quasiparticle and molecular parts, **thermodynamically consistent** equation of state
 - entropy balance H-theorem, explicit **two-particle correlated entropy**
 - thermodynamic observables functions of **nonequilibrium distribution**
2. Model of Maxwellian particle with contact interaction:
 - ratio of energy gain to external power feed = ratio of latent heat to interaction
 - universal critical ratio of scattering length to DeBroglie wavelength
 - correlation cooling and heating
3. Successfully applied to: heavy ion collisions, deep neutral impurities, Bernoulli potential at superconducting surfaces, ...

Literature: <http://www.k-morawetz.de>

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KLAUS MORAWETZ
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